Advanced Polyolefin Separators for Li-ion Batteries Used in Vehicle Applications

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Project ID: ES289

OVERVIEW:

Timeline:

- Start Date: June, 2015
- End Date: December, 2017
- 80% Complete

Project Goals to Address Barriers:

- Improved energy density:
  - Voltage oxidation resistance up to 5V
- Improved abuse tolerance:
  - High temperature dimensional stability above 180°C
  - Shutdown Features
- Reduced Cost

Budget:

- Total Project Funding (50/50)
  - USABC Share: $1,042,745
  - ENTEK/Farasis Share: $1,042,745
- FY16 Funding:
  - USABC Share: $536,504
  - ENTEK/Farasis Share: $536,504

Partners/Subcontractors:

- Farasis Energy
- Mobile Power Solutions

RELEVANCE AND PROJECT OBJECTIVES:

Relevance:

- Mass adoption of electric vehicles requires improved lithium ion cell performance, improved safety, and reduced cost. This project addresses these challenges through inorganic filled and ceramic coated separator development.

Project Objectives:

- Improve energy density
  - High voltage oxidation resistance up to 5 V.
- Improve cell abuse tolerance with the following separator features:
  - High temperature dimensional stability above 180°C.
  - Shutdown
- Reduce separator cost through:
  - Reduced electrolyte fill times, by improving separator wetting by electrolyte solution.
  - Reduced materials costs of coatings, by minimizing coating mass required to reach high temperature dimensional stability.
  - Reduced manufacturing costs, by developing coating technologies that can be implemented continuously in-line with base separator production

MILESTONES:

Date	Milestones	Status
October, 2015	Production trial for reduced shutdown temperature: **8°C reduction in shutdown temperature**	Complete
December, 2015	Production trial for inorganic filler screening: **>20% improvement in wetting (USABC Target)**	Complete
December, 2015	USABC Separator Deliverables 1 and 2 sent to Farasis Energy for cell testing	Complete
February, 2016	Production trial for silica loading level optimization: **Achieved porosities greater than 60%, Mac Mullin Number less than 4 (USABC target for power cells)**	Complete
August, 2016	Finalized design for 4.4V NMC 622 cells. Cells built with both inorganic filled and ceramic coated separator.	Complete
December, 2016	Demonstrated improved cycle life, reduced self discharge, and reduced capacity fade in 4.4 V cells using ENTEK ceramic coated separator.	Initial evaluation complete. Further cell performance evaluation underway.
January, 2017	Development of electrolyte systems for 4.9-5.0 V HVS cells	Underway
February, 2017	Coated separator delivered to Farasis production facilities for HVS cell development.	Complete

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APPROACH AND STRATEGY:

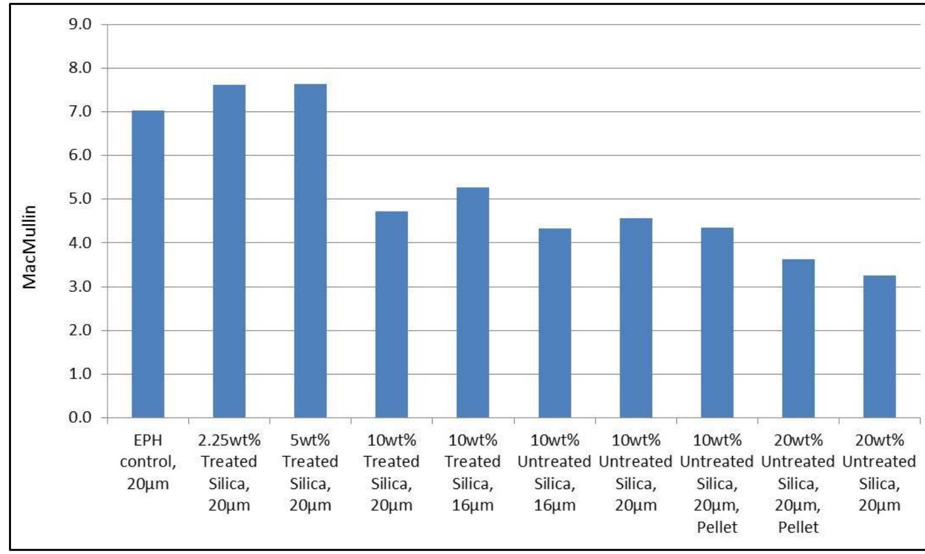
- **Phase 1**: Build in the features with inorganic filler and ceramic/polymer coatings
  - Improve wetting, ionic conductivity, voltage oxidation resistance, and safety features (low shrinkage, shutdown)
- **Phase 2**: Take out the cost
  - Reduce electrolyte fill time, demonstrate in-line coating technologies, optimize coating to minimize material costs
- **Phase 3**: Demonstrate technology in large format cells

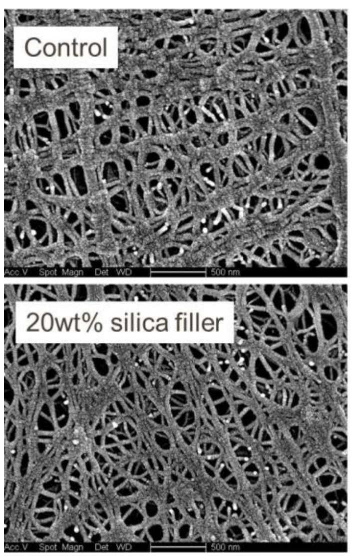
Phase 1	Phase 2	Phase 3
Build in the Features Base Membrane Optimization for Porosity and Wettability → Inorganic Filler Loading for Higher Porosity and Wettability → Coatings for Abuse Resistance, Shutdown Enhancement and Voltage Stability 9 months	Take out the Cost: High throughput coating 9 months	Demonstrate in Deliverable Cells Prismatic Pouch 25 Ah 5V 8 months

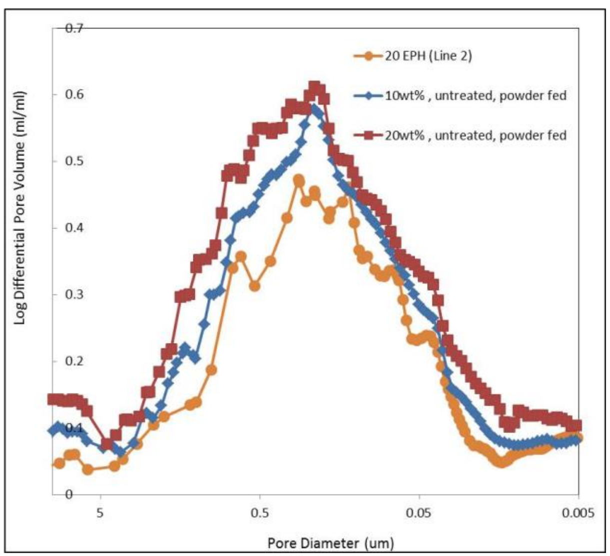
Pilot coating line at ENTEK

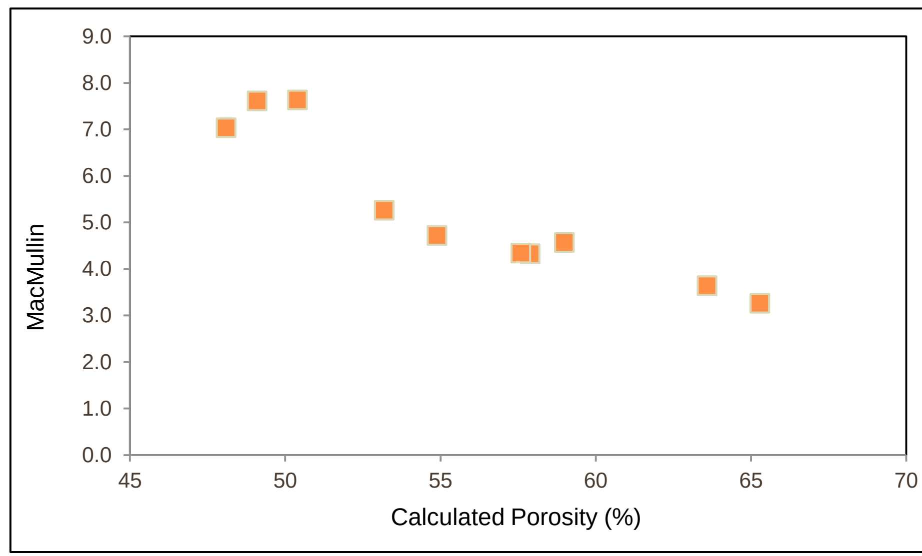
TECHNICAL PROGRESS: SILICA FILLED IONIC CONDUCTIVITY

- For given process conditions, ionic conductivity increased (decrease in MacMullin) with increasing silica loading level
- At 20 wt% loading levels, the MacMullin Number was below 4 **(USABC goal for power applications)**
- Direct correlation between ionic conductivity and separator porosity
- Despite much higher porosity, the inorganic filled separator pore size was similar to that of the control sample









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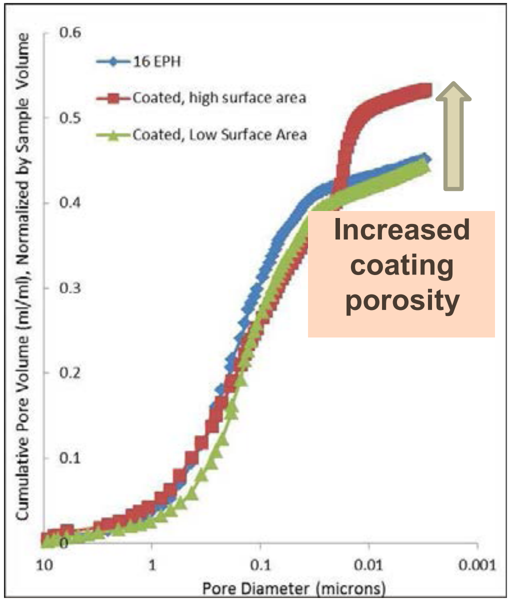
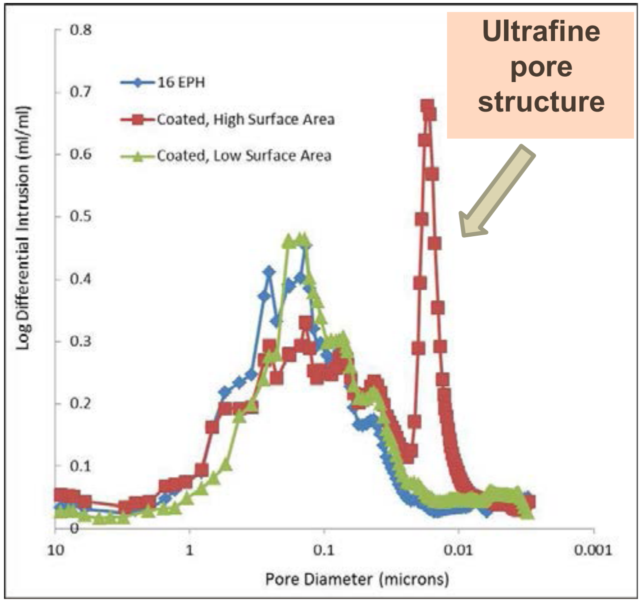
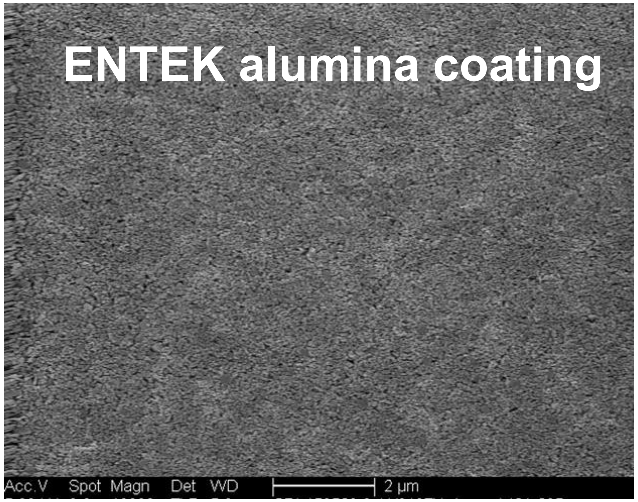
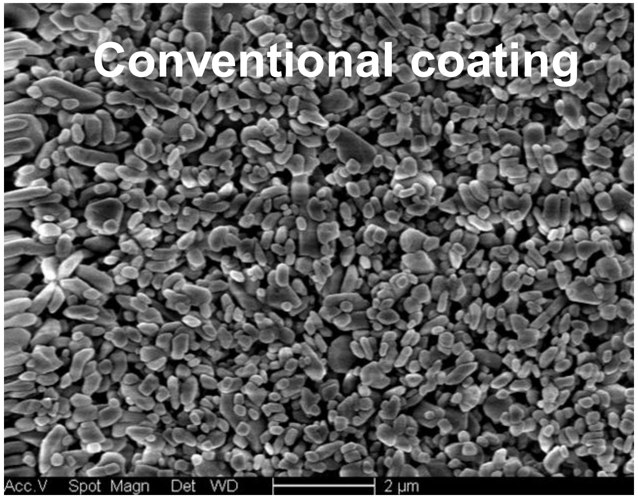
TECHNICAL PROGRESS: COATED SEPARATOR DEVELOPMENT

- ENTEK's approach: alumina coatings with nanostructure, high surface area
  - Excellent dimensional stability, improved safety
  - Very thin, uniform coatings can be applied for improved energy density
- Challenge:
  - Higher moisture content than conventional coated separator









- ENTEK uses nano-particulate alumina with ultrafine pore structure to improve safety

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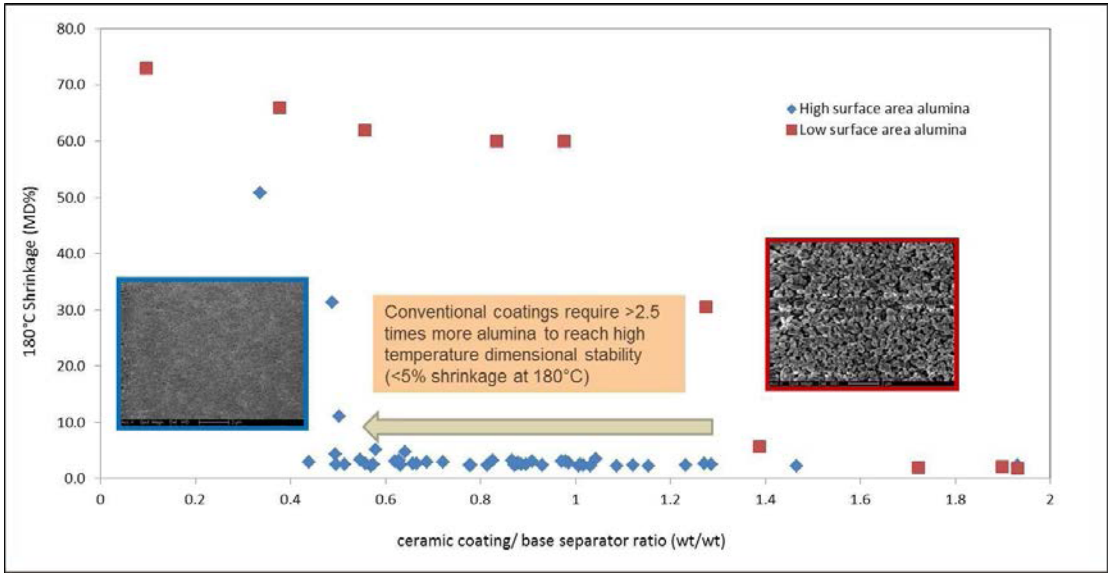
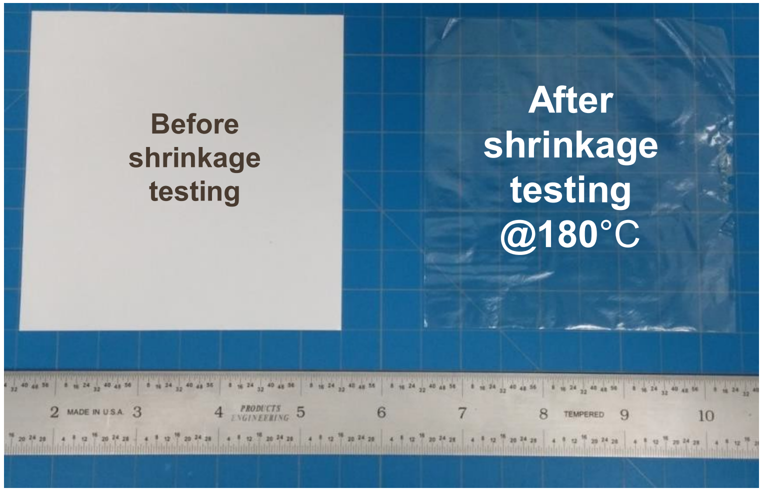
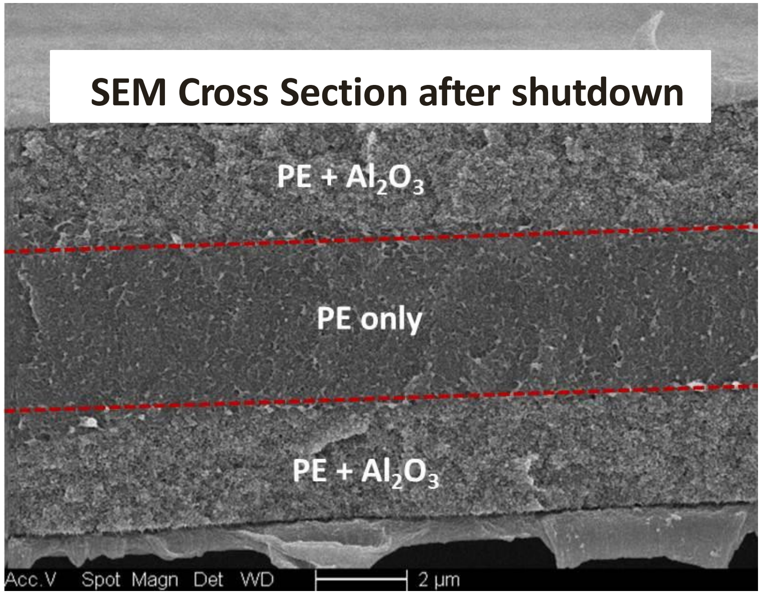
TECHNICAL PROGRESS: COATED SEPARATOR SAFETY FEATURES







- ENTEK's nanoparticle alumina coated separator yields improved high temperature dimensional stability (<5% shrinking at 180°C) and shutdown features.
- Only ~40 wt% of alumina required for desired properties compared to conventional coated separator.
  - =>cost reduction
  - =>improved energy density (thinner separator)
  - => reduced manufacturing costs (reduced wet layer thickness)

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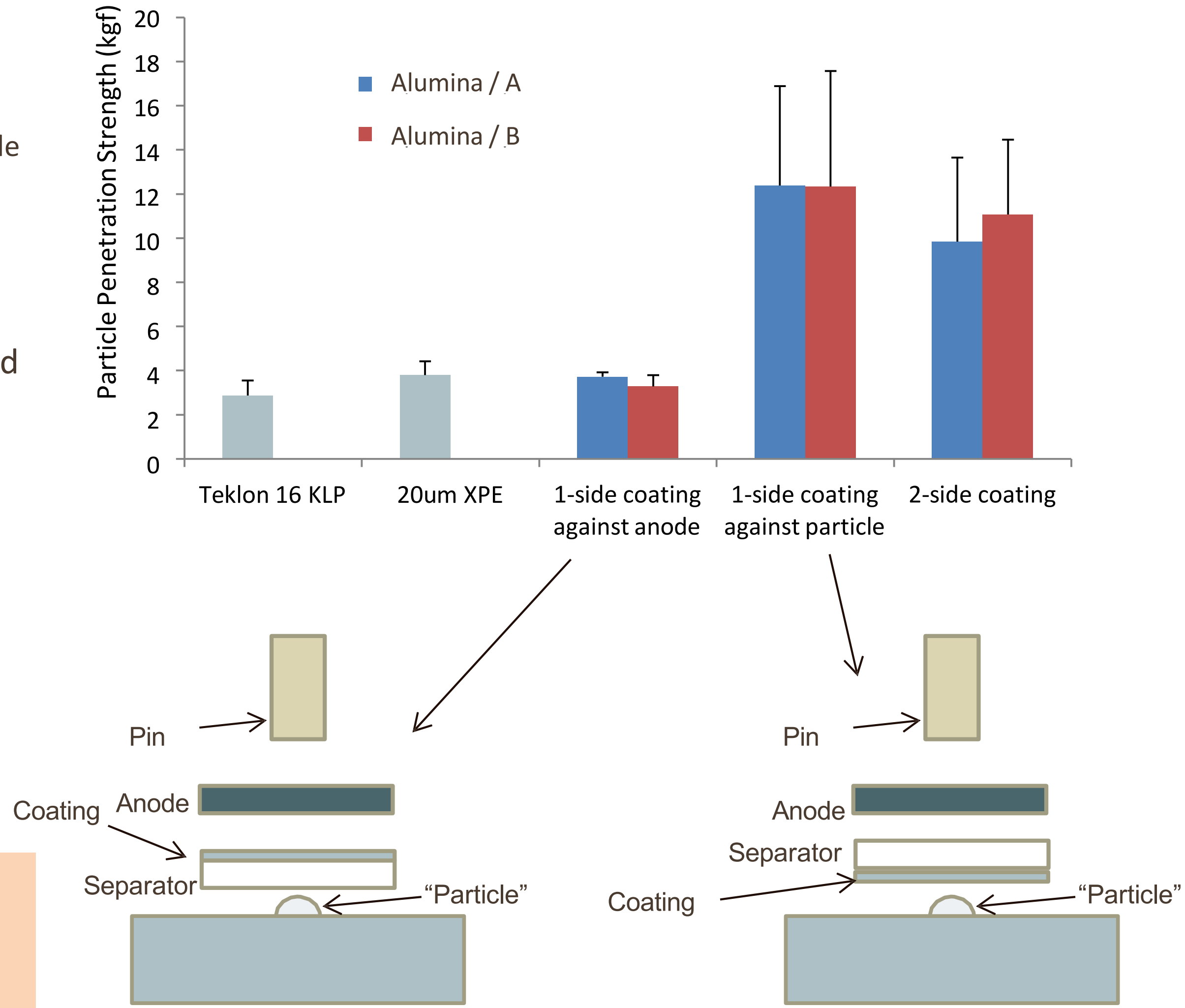
TECHNICAL PROGRESS: PARTICLE PENETRATION RESISTANCE

- Testing was performed under three different configurations:
  - Single side coated separator, ***uncoated*** side against the particle
  - Single side coated separator, with ***coated*** side against the particle
  - Double side coated separator



- For single sided separators, when uncoated side is adjacent to particle, penetration strength is similar to the base material controls
  - Coating is stressed under tension
- However, when the coating is adjacent to the particle, the penetration strength is significantly higher than controls
  - The coating is largely compressed

Double sided coated separator offers better protection against particle penetration

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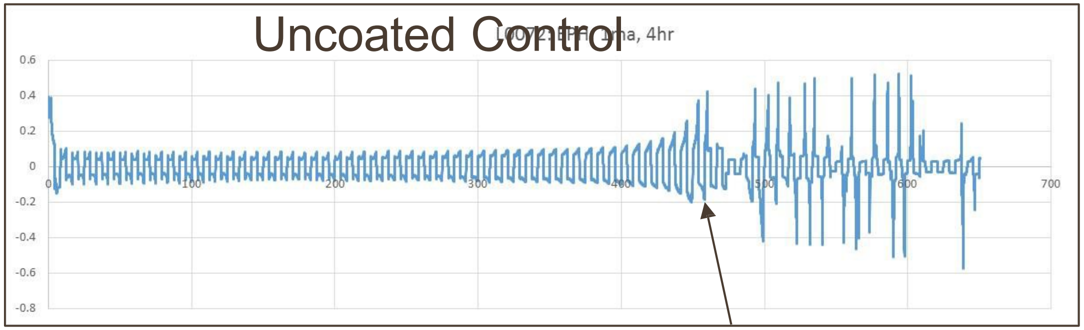
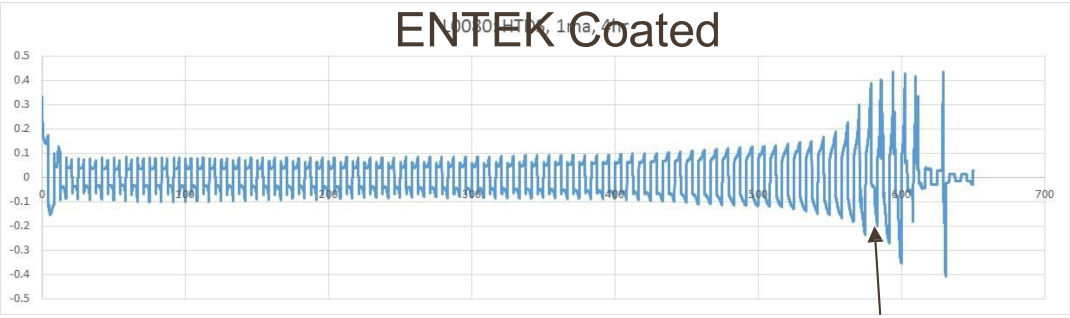
TECHNICAL PROGRESS: DENDRITE GROWTH SUPPRESSION

- Coin cells were built with two lithium electrodes:
  - Pan/SS disk/Li foil/separator/Li foil/ SS disk/Belleville washer/lid
  - Electrolyte= 1M $LiPF_6$ in 1:1 EC:EMC
- The key metric: the time before lithium dendrite shorting.



Cell voltage under load drops after 474 hrs.



Cell voltage under load drops after 579 hrs.

- Symmetric cell data indicate improved resistance to dendrite growth in cells built with ceramic coated separator

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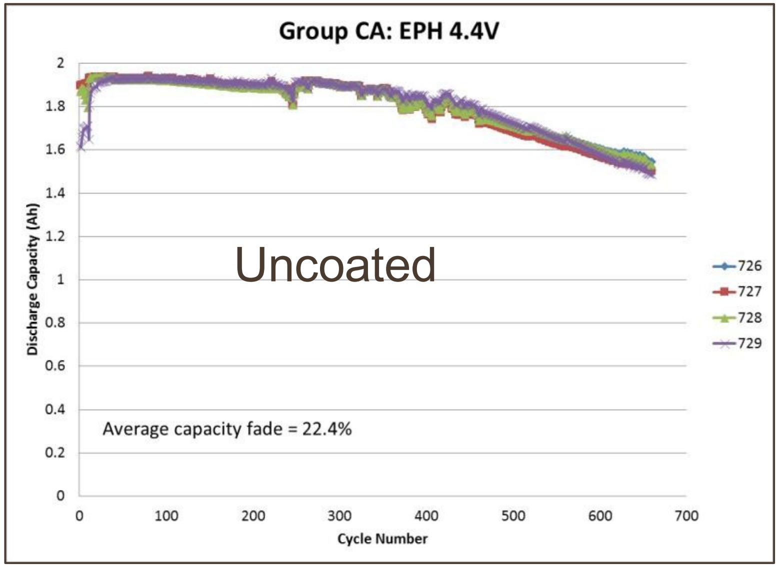
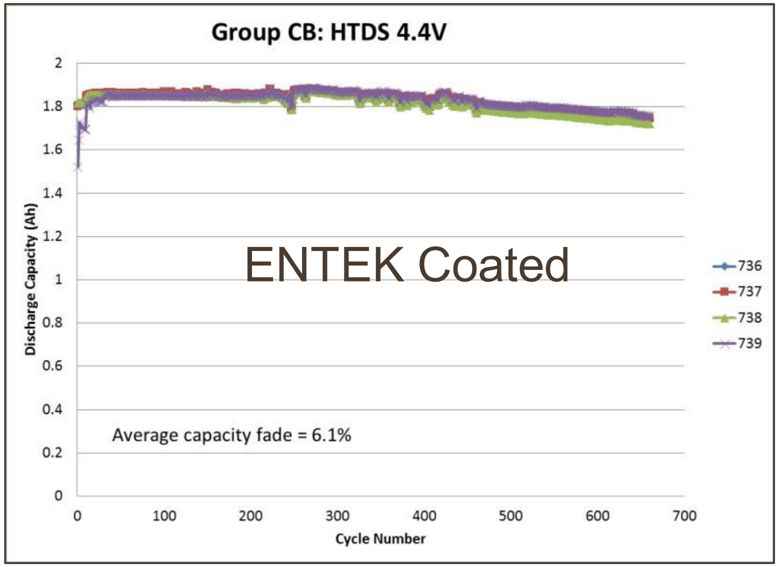
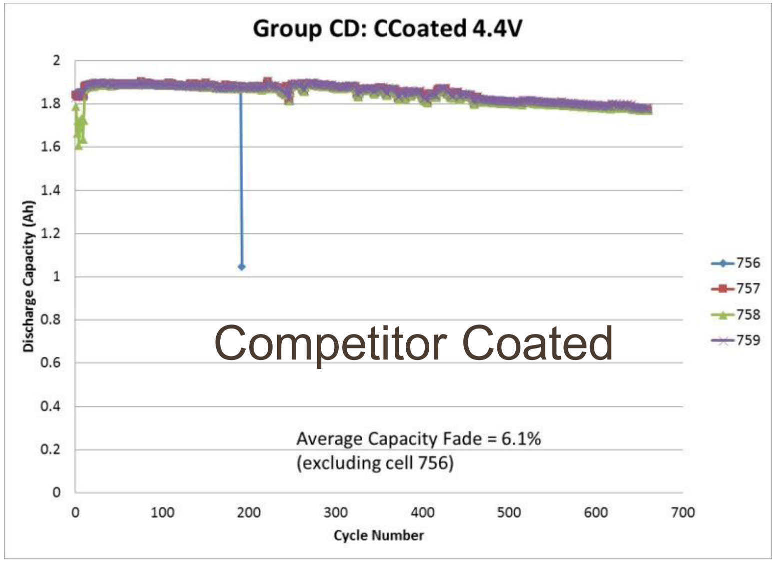
TECHNICAL PROGRESS: CYCLE LIFE OF 4.4V, 622 NMC CELLS

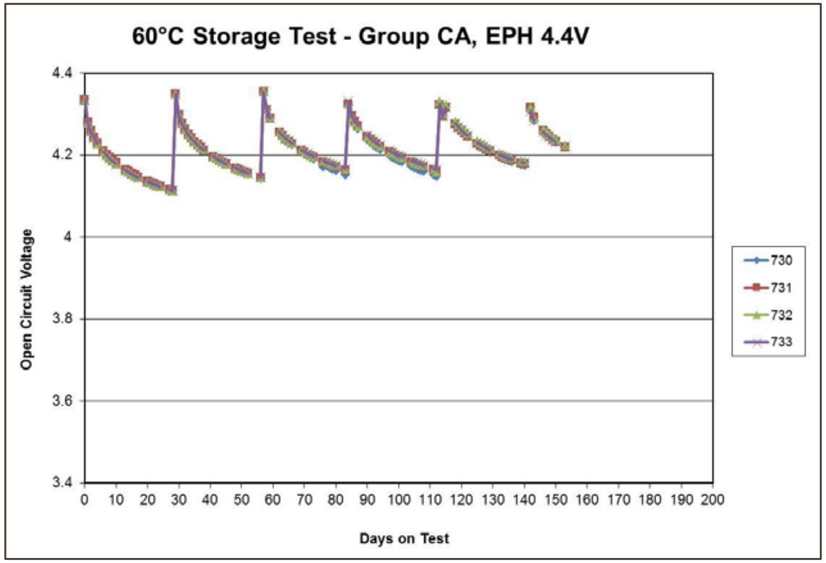


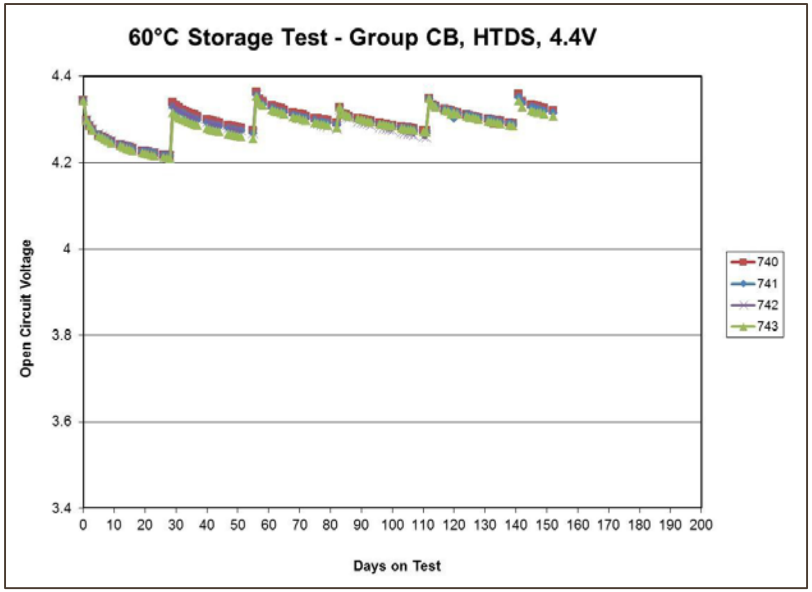


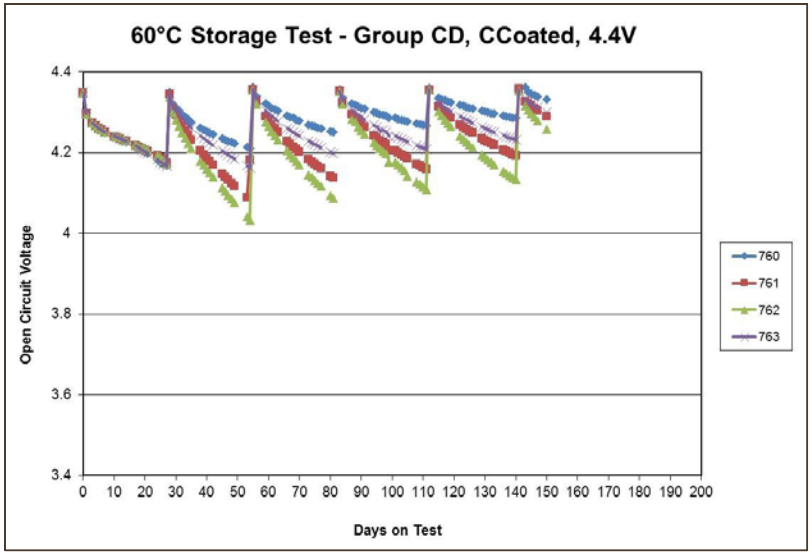
- ENTEK's alumina coated separator shows much improvement in cycle life compared to cells built with uncoated control separator.
- Comparable to competitor coated separator.



TECHNICAL PROGRESS: 60°C STORAGE TESTING

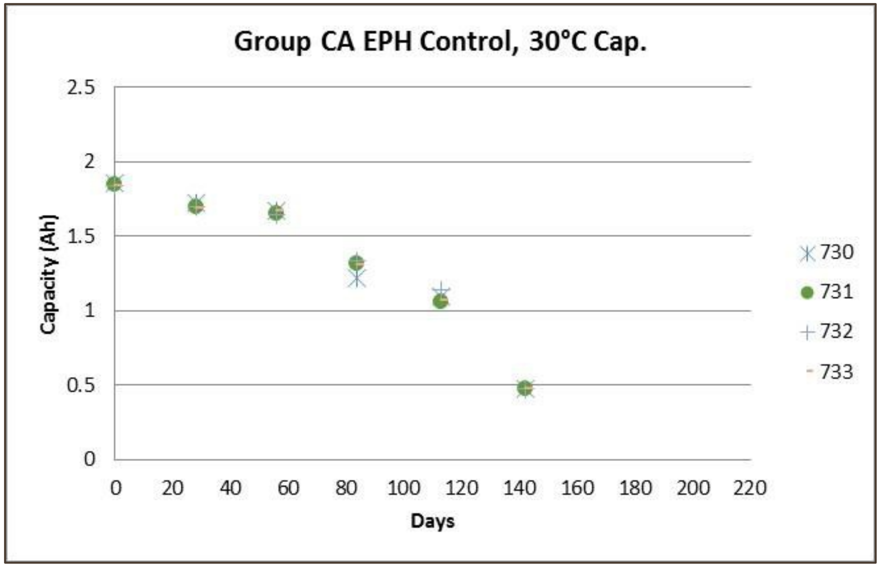


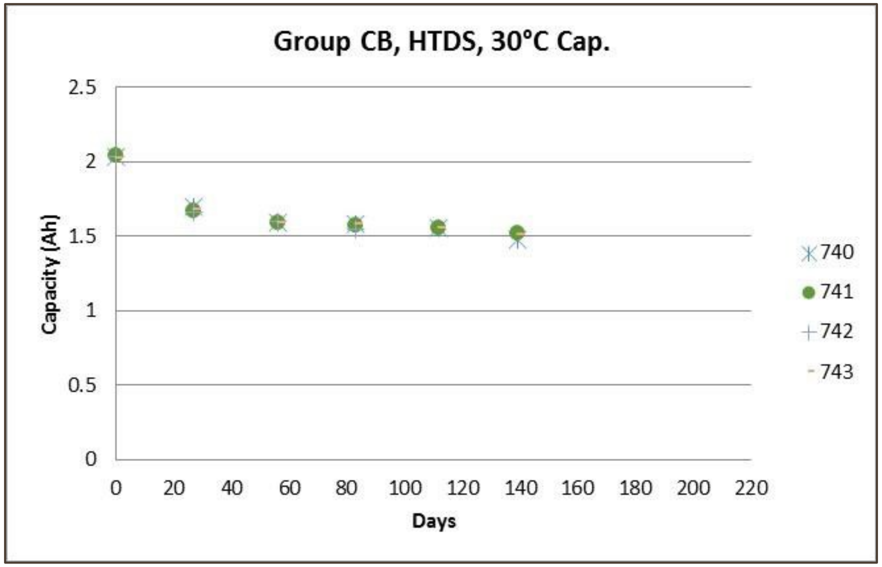




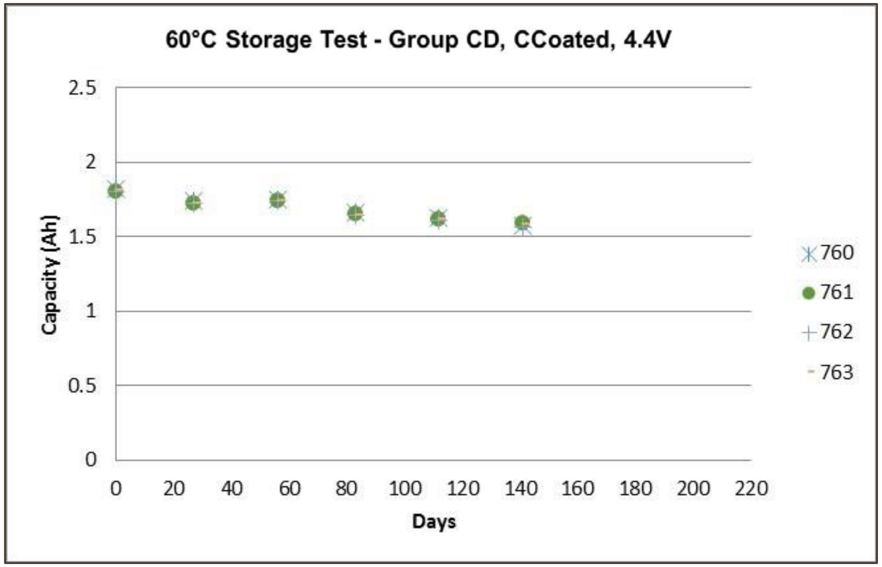
- ENTEK's alumina coated separator shows reduction in self-discharge compared to both uncoated and competitor coated separators.
- Much improved consistency compared to competitor coated separator.

TECHNICAL PROGRESS: CAPACITY FADE, 60°C STORAGE TESTING

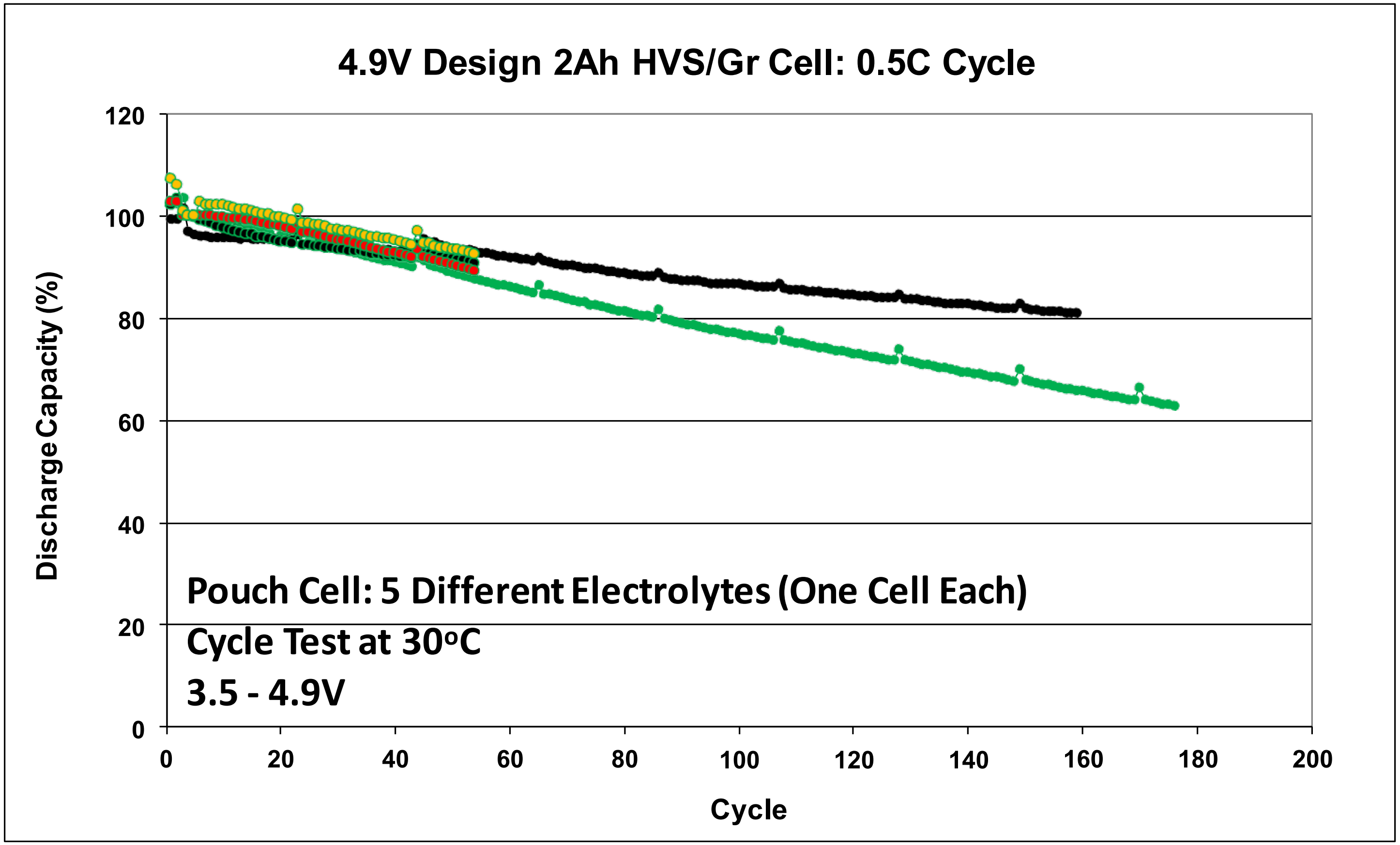




- After 60°C storage testing, ENTEK's alumina coated separator shows much improvement in capacity fade compared to cells built with uncoated control separator.
- Comparable to competitor coated separator.



TECHNICAL PROGRESS: 4.9V HVS CELL DEVELOPMENT



- Various electrolyte systems have been evaluated for optimization in 4.9 V HVS cells.
  - Cells presented here were all built with polyethylene base separator.
- Evaluation of various coated separators integrated into HVS cells is currently under way.

RESPONSE TO COMMENTS FROM PREVIOUS YEAR

- Reviewer 2: "…a link of production methods costs needs to be discussed and the cost cannot be addressed by only linking it to cell fill time."
- **Response**: Improved wetting is only a small contribution to the overall benefits of ENTEK's approach for ceramic coated separator. As described in last year's presentation and reiterated here, there is a **60wt% reduction** in ceramic coating material required for the desired properties using ENTEK's approach compared to conventional ceramic coated separator. The cost benefits are:
  - Reduced materials costs
  - Improved energy densities (thinner separator requirements)
  - Potential for faster coating speeds (reduced wet layer thickness), and thus manufacturing costs
- ENTEK has also been pursuing advanced coating methods to increase coating throughput, with the potential to coat separator with base separator production, rather than as secondary step.
- Reviewer 2: "…there are no cell measurements."
- Response: ENTEK has included 4.4V cell performance data, comparing ENTEK's ceramic coated separator to competitors. 5.0V cell development is currently underway.
- Reviewer 2: "…Farasis' role was not active at the moment."
- Response: ENTEK has been actively engaged with Farasis in optimizing the 4.4V cell design. We are currently working diligently with Farasis on the new 4.9-5.0V cell design.

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PARTNERSHIPS AND COLLABORATIONS

- **Farasis Energy** (Project Partner)
  - High voltage cell development
  - Cell builds for separator development

- **Mobile Power Solutions**
  - Subcontractor for cell performance testing

CHALLENGES AND BARRIERS

- Development of separators for high voltage cells
  - Requires the proper selection and integration of electrodes, electrolyte, ***and*** separator
  - Optimization of the separator properties is only a small portion of what is required to have a fully functional high voltage cell >4.5 V. Electrolyte is key in development.

- High moisture in high surface area alumina coated separator
  - Various methods for removing moisture, such as drying/packaging, formulation change, or surface modification will be evaluated.

- In-line coating for reduced costs
  - Requires specific coating speeds and path lengths for a given production line. Technical and economic feasibility for in-line coating will be addressed in the upcoming months.

PROPOSED FUTURE WORK

- **Continue to evaluate voltage oxidation resistance of alumina/polymer coated separator**
  - Integrate the optimized ceramic coated separator with a high voltage cathode and electrolyte into an operating cell.

- **Further develop 4.9-5.0 V HV Spinel cells with Project partner Farasis Energy.**
  - Further optimize electrolyte system
  - Evaluate various ceramic coated separator in 2Ah 18650 and pouch cells.
  - Based on 2Ah testing results, decide go/no go on large format, 25Ah cells.

- **Demonstrate coating technologies that improve throughput and can be integrated with base separator production for reduced cost**
  - Compare coating methods (e.g. immersion, slot, gravure coatings) and drying techniques (for example, conventional, IR, RF and UV drying).

SUMMARY:

Inorganic filled separator development:

- Incorporating inorganic filler into the separator resulted in:
  - Wetting improvement greater than 20% (droplet)
  - Mac Mullin Number less than 4
  - Pore size distribution similar to unfilled control samples

Coated separator development:

- Coating the base separator with a high surface area alumina resulted in:
  - High temperature dimensional stability (<5% shrinkage @180°C)
    - Less coating required to reach high temperature dimensional stability compared to conventional alumina coatings
  - Wetting improvement greater than 50% (droplet)
  - Improved cycle and calendar life compared to uncoated control.

- Future work will include further evaluation of separator voltage oxidation residence, development of 4.9-5.0 V HVS cells utilizing ceramic coated separator, and demonstrating coating techniques for reduce cost.

TECHNICAL BACK-UP SLIDES

BACKUP SLIDE: SILICA FILLER CONCENTRATION

- Silica filler was further evaluated at concentrations up to 20 wt% loadings
  - Untreated vs. silane-treated silica
  - Powder vs pellet fed

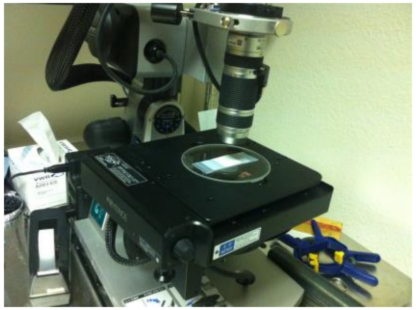
F.O.	GEM Set #	Sample Description	Filler Feed type	Porosity	Calculated Thickness	Basis Weight	Gurley Number	Puncture	120°C shrinkage 30 min	120°C shrinkage 30 min	MD Tensile	XMD Tensile	MD Elong.	XMD Elong.
				%	µm	g/m^2	s/100cc	gf	MD	XMD	kg/cm^2	kg/cm^2	(%)	(%)
1996	4	EPH control, 20µm	-	48.1	19.80	9.9	179	571	14.1	9.8	1163	773	79.0	272
1996	6	5wt% Treated Silica, 20µm	Powder	50.4	20.25	9.9	154	533	14.8	9.6	1154	722	75.0	263
1996	7	10wt% Treated Silica, 20µm	Powder	54.9	20.12	9.2	121	511	15.6	13.1	1142	725	81.3	238
1996	8	10wt% Treated Silica, 16µm	Powder	53.2	16.6	7.9	112	455	15.5	12.6	1014	765	62.8	206
1996	9	10wt% Untreated Silica, 16µm	Powder	57.9	14.2	6.1	84	347	13.1	13.1	1011	711	50.3	222
1996	10	10wt% Untreated Silica, 20µm	Powder	59.0	20.9	8.7	95	440	16.2	11.9	815	722	72.8	198
1996	11	10wt% Untreated Silica, 20µm, Pellet	Pellet	57.6	20.7	8.9	95	452	14.9	11.0	850	720	87.8	291
1996	12	20wt% Untreated Silica, 20µm, Pellet	Pellet	63.6	22.7	8.9	67	379	14.9	13.7	818	619	72.3	277
1996	13	20wt% Untreated Silica, 20µm	Powder	65.3	20.63	7.8	75	393	17.4	14.0	803	532	57.0	241

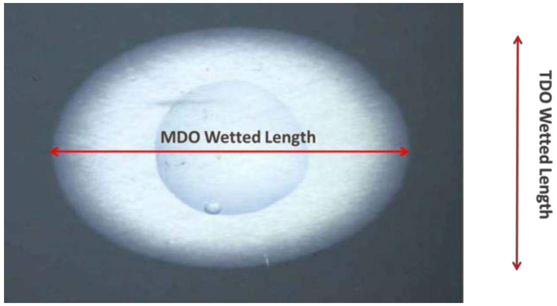
- Increasing filler loading level resulted in:
  - Increased porosity
  - Decreased Gurley Numbers
  - Decreased mechanical properties
    - Comparable to commercial product. Still within USABC Target
- Pellet fed, untreated silica showed the best sheet quality

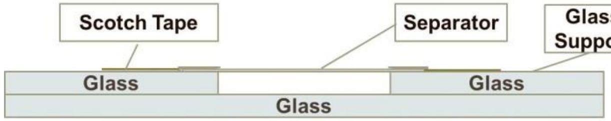
BACKUP SLIDE: SILICA FILLER WETTING IMPROVEMENT

Droplet Wetting Method:

- Separator suspended in air to prevent solvent wicking on glass
- 5ul droplet placed on separator by micro-pipette. Wetted area measured after **5 minutes**.
- Solvent: propylene carbonate/tri(ethylene glycol) dimethyl ether = 1/1 (vol.)

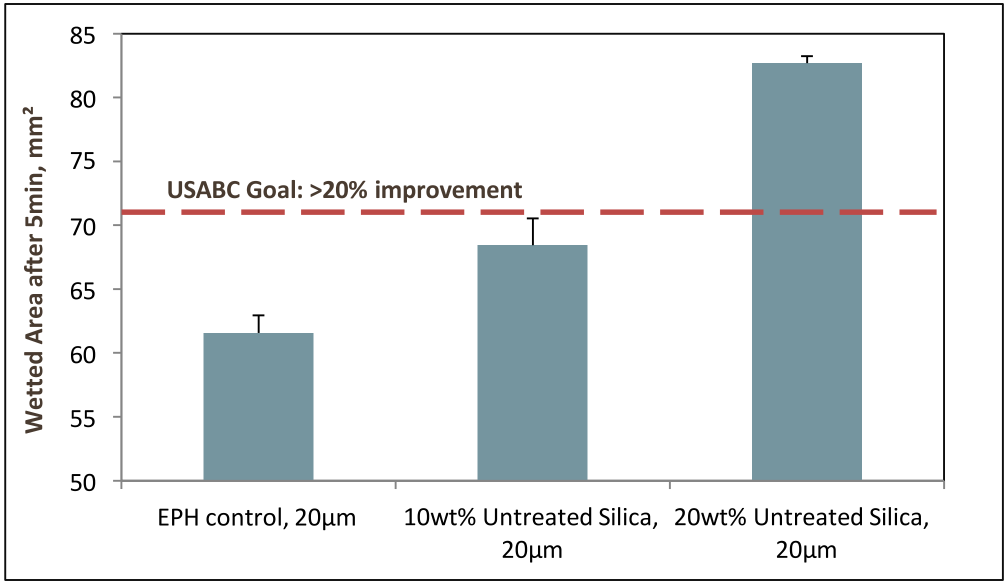






Results:

- Inorganic filled separator with 20 wt% loading showed a ***34% improvement in wetting*** in the droplet wetting test



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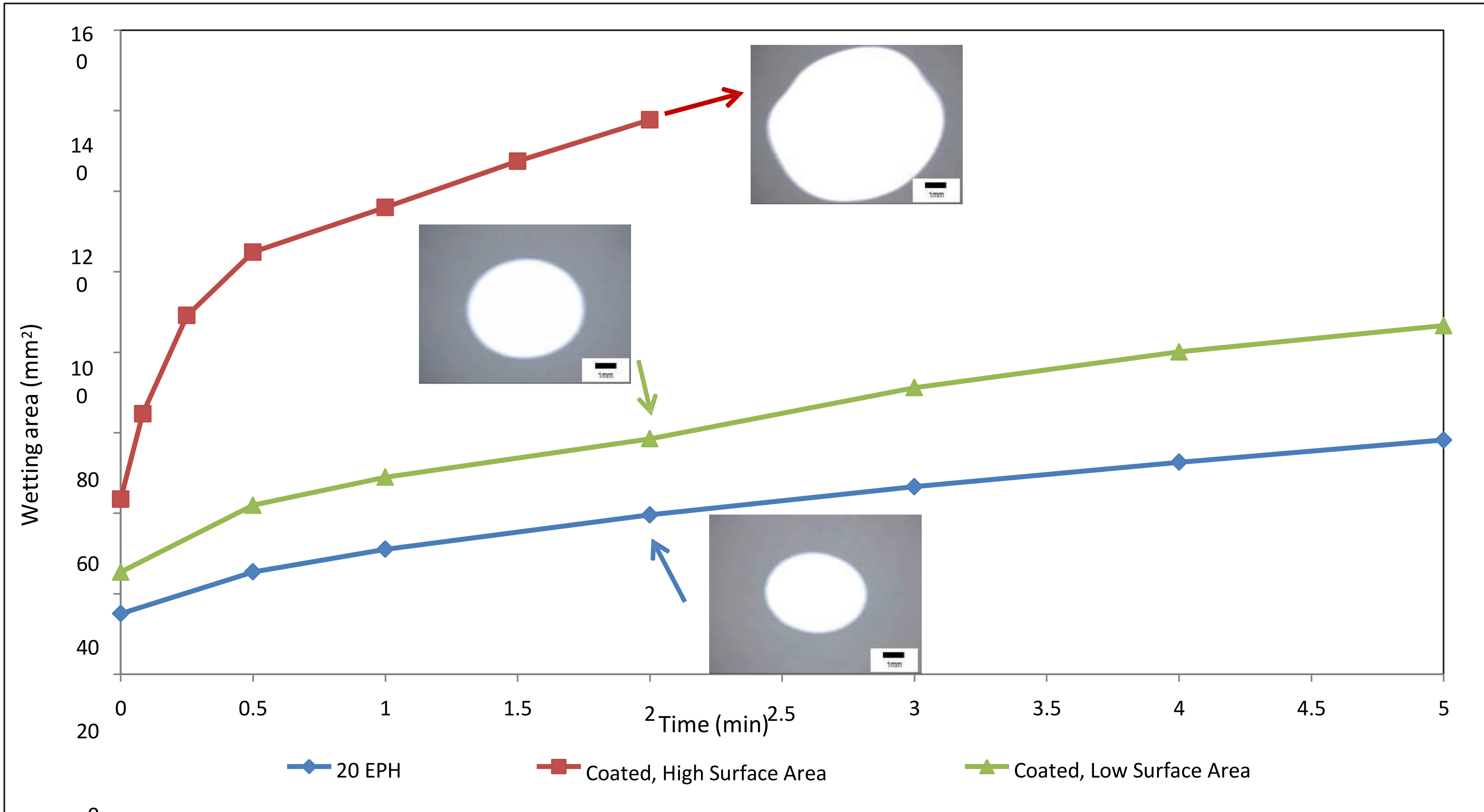
BACKUP SLIDE: COATED SEPARATOR WETTING



- Electrolyte filling is often a bottleneck in cell manufacturing
- Separator coated with high surface area, alumina nanoparticles shows excellent wetting

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